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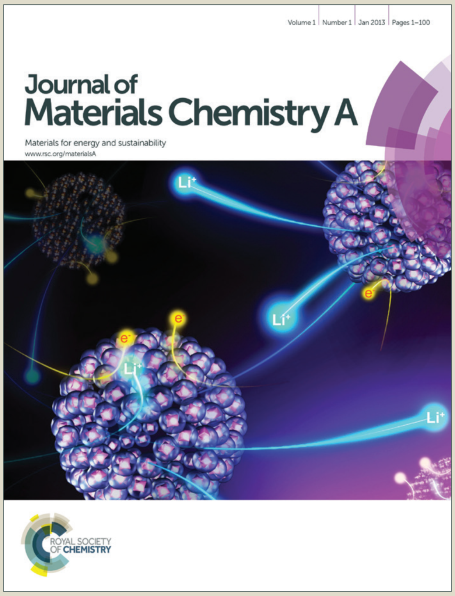

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Integration of Si in Metal Foam Current Collector for Stable Electrochemical Cycling in Li-ion Battery

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Here we designed and fabricated an integrated Li-ion battery electrode by trapping the electrochemical active materials inside a three-dimensional (3D) metal current collector. Silicon microparticles have been sealed into a compressed 3D Cu foam matrix, which has interconnected pores for electrolyte wetting and also providing enough empty space for the volume expanding of Si during lithiation. Such electrode design can effectively trap the active materials inside the metal framework during dynamic electrochemical cycles, preventing particles escape from the current collector. Taking these advantages, the electrode exhibits greatly improved electrochemical stability. The initial capacity reaches 2500 mAh/g and kept more than 1000 mAh/g over 200 cycles. While setting a constant charge capacity by 500 mAh/g, the capacity does not reduce after 600 cycles.

Introduction

The fast-growing demands of portable electronics, electric drive vehicles and grid-scale energy storage stations require lithium-ion batteries with high energy and power densities. Graphite, the traditional anode material in lithium-ion batteries does not meet with the high energy needs due to its limited theoretical specific capacity of ~370 mAh/g.[1-2] Alloy type anodes such as silicon are promising alternate electrode materials according to their high lithium storage capacity per unit mass and per unit volume, because of their ability to reversibly incorporate a high concentration of Li atoms.[3-5] However, during continuous lithium insertion/extractions, such electrodes usually suffer from dramatic volumetric and structural changes which cause not only mechanical fracture inside electrode materials, but also electrical disconnection between active material and current collector. As a consequence, the severe capacity fading during cycles presents a significant technical challenge.[6-11] Accordingly, many studies have been conducted to improve the electrochemical stability of silicon-based lithium-ion battery anodes.[12] Recently, exciting progress has been made through designing and constructing nanostructured silicon. Nanocrystals[13], nanowires[14-15], core-shell nanofibers[16-17], nanotubes[18-20], nanospheres[21], nanosheet[22], nanoporous materials[23-26] and Si/carbon nanocomposites[27-31] have shown longer cycling life as candidate anode materials compared with micron-sized Si particles. Despite significant improved cycling performance of nanostructured Si electrode, preparation of nano-sized Si either requires chemical/physical vapour deposition or involves complicated processes, leading to costly, low-yield synthesis and low tap density that is difficult to scale up to practical levels[32]. Micro-sized Si powders are favourable for practical battery applications since they often enable lower manufacturing cost and higher tap density than nanosized materials. However, the disadvantages of Si microparticles as electrodes are obvious. Micro-sized Si are more likely to undergo disintegration upon volume change during lithiation/delithiation compared with nanosized materials, resulting in severe capacity fading.[33] Cho and Park et al. reported a method to synthesize micro-sized porous Si-C composites by chemically etching followed by carbon coating. This micro-sized porous Si-C composites exhibited good electrochemical performance within 70 cycles.[34-35] Park et al. reported an approach to produce micro-sized, carbon-coated Si-SiO-SiO_2 three-component anodes consisting of Si/SiO cores and crystalline SiO_2 shells. This micro-sized multicomponent anodes show a high reversible capacity and good capacity retention.[36] Recently Wang et al. reported a micro-sized Si-C composite composed of interconnected Si and carbon nanoscale building block, a high electrochemical performance was achieved.[32] Despite encouraging results achieved, these micro-sized Si anode materials still employ nanoscale building blocks. Between these and other reports, there are still few efficient and scalable approaches for preparing micro-sized silicon anodes without nanoporous complex structure and/or coatings.

Among major battery components, current collectors have not been the centre of attention compared with other electrochemical active materials.[37] Conventional way to fabricate electrodes is to simply coat the active electrode particles slurry onto a flat current collector such as copper or aluminium foils. Polymer binders are employed to enhance the cohesive strength between electrode particles and the current collector.[38] Such electrode structure is widely accepted, however, for alloy type electrode material systems, the huge volume and structural changes accompanied with lithiation and delithiation will easily lead to particles pulverization and further cause the detachment of active materials from current collector, leading to electrical disconnection as illustrated in Figure 1a. Such electrical disconnection directly results in a rapid capacity decay of the whole electrode. Obviously, a reliable electrical connection between electrode material and metal current collector during dynamic electrochemical cycles is critical to achieving long cycle life of Si microparticles. By considering this, we designed an electrode structure by sealing Si microparticles inside metal current collector as integrated electrode as shown in Figure 1b. Very different from traditional electrode design, the metal current collector serves not only for providing a physical support and conducting path through the electrode material, but also as a porous and tight framework for trapping active powders inside, preventing material detachment from the substrate (Figure 1b).

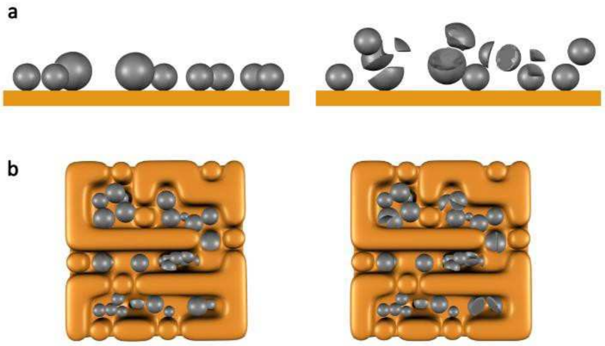

Fig. 1. Schematic show of battery electrode design. (a) Traditional electrode structure. Silicon particles crack and lose connection with current collector during cycling. (b) Integration design of silicon particles and current collector. While the silicon particles expend and even crack, the active materials are still stuck in the 3D current collector to keep contact.

Experimental

Electrode synthesis

We prepared the integrated electrode structure following the steps described in Figure 2b. We started the electrode fabrication from commercial available nickel or copper foam, which is light weight, low cost and can be generated in large scale (Figure 2a and b). Silicon particles with a size of around 4 μm (Ronghua Silicon Industry, Shandong, China) were dispersed in ethyl alcohol with concentration of 20 mg/ml. Conventional copper foam (Lifeixin, Shenzhen, China) was cut into square shape with a size of 0.5cm×0.5cm. The copper foam piece was then immersed into the Si suspension and kept for an hour. The electrode was subsequently dried in air in an oven at 60 ^{o}C. The liquid suspension can easily wet out the porous metal foam, carrying active Si particles loaded inside the metal framework through the large pore in the foam (Figure 2c). By repeating these simple processes for several times, certain amount of Si microparticles were loaded inside the metal foam. Note that the initial metal foam had interconnected holes with size of several hundred micrometers, and the Si microparticles loaded inside porous metal by this process can only have loose contact with the metal foam. As a result, the Si particles are not sealed inside the large holes and can be easily detached from the metal substrate during electrochemical cycling. To solve this problem, we pressed the electrode to seal the silicon particles inside the metal foam by a simple calendaring process (Figure 2b) by a calendaring machine (MTI, Hefei, China). It is known that copper and nickel have a good roughness and deformability. A calendaring process can heavily impact the porous metal foam to form a thin sheet electrode which insures the silicon particles sealed inside tightly and can keep close contact with the current collector. The pressure applied was 20 MPa during the calendaring and the copper foam was pressed from the thinkness of 1.9 mm to 90 μm. The electrode was subsequently cleaned by ultra-sonication to remove the silicon particles which were loosely attached on the surface of the metal. The cleaning process was repeated for 3 times. Integrated electrode with Si micronparticle mass loading of 4 mg/cm^2 was fabricated after drying in a vacuum oven at 80 ^{o}C overnight. According to this simple treatment, most Si particles have been trapped inside the metal electrode, however, certain amount of the Si particles were not sealed inside the metal framework, but attached on the out surface of metal sheet. The Si particles adhered on the out surface of metal electrode can easily escape from the substrate during electrochemical cycling and therefore may result in capacity decay. Therefore, we removed silicon particles that adhered loosely on the out surface or trapped loosely by ultra-sonication, cleaning the electrode in ethanol alcohol. We noted that the metal foam would form a porous framework after calendaring, leaving micron sized tunnels interconnected from surface to the inner electrode, leaving open pores of about several micrometers outside (Figure 2d).

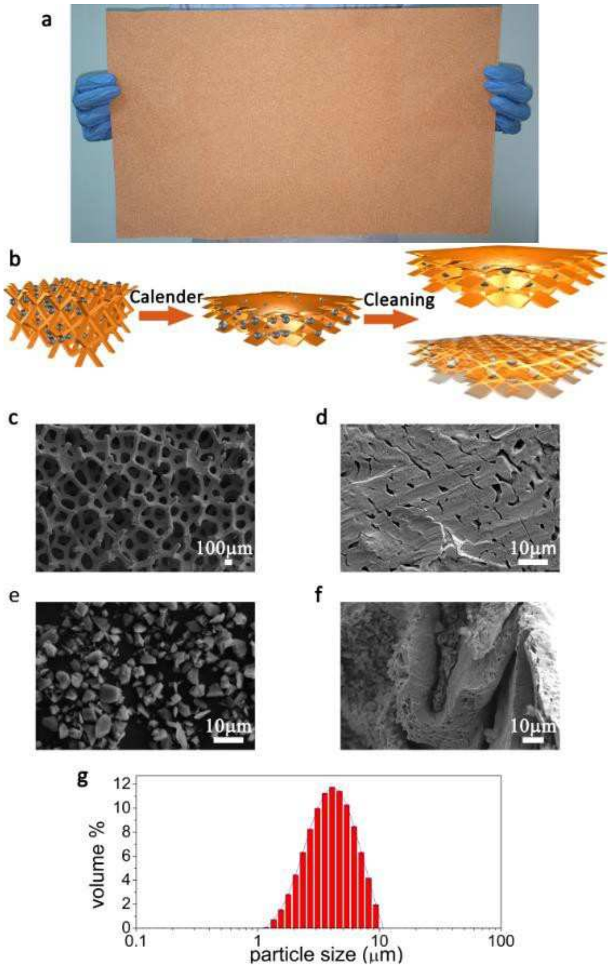

Fig. 2. Fabrication procedures and characteristics of Si/Cu integrated electrode. (a) Photo image of the copper foam used for electrode fabrication. (b) The steps of the integrated electrode for trapping silicon particles. (c) SEM image of initial 3D copper frame. (d) After calendaring, the surface of the electrode becomes flat. (e) SEM image of the silicon microparticles. (f) The cross section of the Si/Cu integrated electrode. (g) The size distribution of silicon particles, the average particle size is 4 μm.

Taking advantages of the porous electrode structure, electrolyte can easily wet inside the electrode and reach the surface of silicon particles through the interconnect tunnels. Another obvious advantage for the porous electrode is that the empty space between metals can provide enough volume to contain the expansion of silicon materials after lithiation. Meanwhile, the silicon materials, which have been heavily pressed and trapped inside metal current collectors, can hold firm contact with the porous metal electrode and can hardly escape from of the current collector through the tiny porous inside metals. We note that the Si particles with micron size cannot prevent materials pulverization during continuous Li insertion and extractions since nanostructures are not designed to release the huge strain of Si materials after lithiation (Figure 2 e and f). However, even the failure of silicon particles, the majority of the Si fragment are still trapped inside the porous metal current collector and maintain electric contact with metal.

Electrochemical characterization

Assemble coins using this silicon anode as working electrode and the Li metal as counter electrode in an argon-filled glove box. Obviously, for an untreated micro-sized silicon anode, during lithiation, the huge internal stress caused by the volume change would result in a more serious crack and pulverization than the nano-sized. [5,13] We chose micron-sized untreated silicon particles as our active materials (Figure 2e and g). To the best of our knowledge, micron-sized Si particles without any inner nanostructure have not been used for high performance Li-ion battery. [12] A 25 μm thick micronporous polypropylene membrane was applied as the separator (Asahi Kasei), 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate/fluoroethylene carbonate (1:1:0.04 vol/vol/vol, Ferro Corporation) was used as the electrolyte and Li foil (MTI) was used as the counter electrode. Electrochemical measurements of the electrode were performed with LIR2032 Coin-type half-cells assembled in an Ar Filled glove box (MB200MOD). All electrochemical measurements were carried out at room temperature. We evaluated the electrochemical performance between 0 and 1V versus Li^+/Li under various rates (BS-9300R/10V2A MTI 8 channels battery analyzer). The CE was calculated as $(C_{delithiation}/C_{lithiation})\times 100\%$, where Clithiation and Cdelithiation are the capacity of the anodes for lithium insertion and extraction.

Results and discussion

In a fully lithiation/delithiation electrochemical test, the traditional electrode with untreated microparticles (~ 4 μm) coating on the copper foil gets an initial delithiation capacity of about 2000 mAh/g; however, the delithiation capacity dropped to only 1485 mAh/g after one cycle. After 20 cycles, the electrode losses over 90% capacities with only less than 200 mAh/g left (Figure 3a). For a 3D integrated electrode, it has an initial delithiation capacity of about 2500 mAh/g. After electrochemical cycles of more than 100 and 200 times, the electrode remains a high capacity of around 2000 mAh/g and 1200 mAh/g, respectively. As comparison, for the electrode using traditional current collector, the serious pulverization and detaching lead active materials loss causing a rapid capacity fading, even when we control the extent of lithiation/delithiation to buffer the deformation. It should be noted that the integrated electrode starts capacity decay after fully lithiation/delithiation for around 100 cycles (Figure 3a). The capacity fading may be because of that alloying and dealloying reactions potentially fracture the solid electrolyte interface (SEI) film due to the large volume change of Si anodes. This agrees with the previous reports of Si anodes and other alloy anodes such as Ni −Sn, Cu −Sb, and so forth.[18, 34] We propose that further surface modifications of Si materials may help to build a stable SEI layer and therefore improve the electrochemical stability of Si-metal integrated electrode.[18]

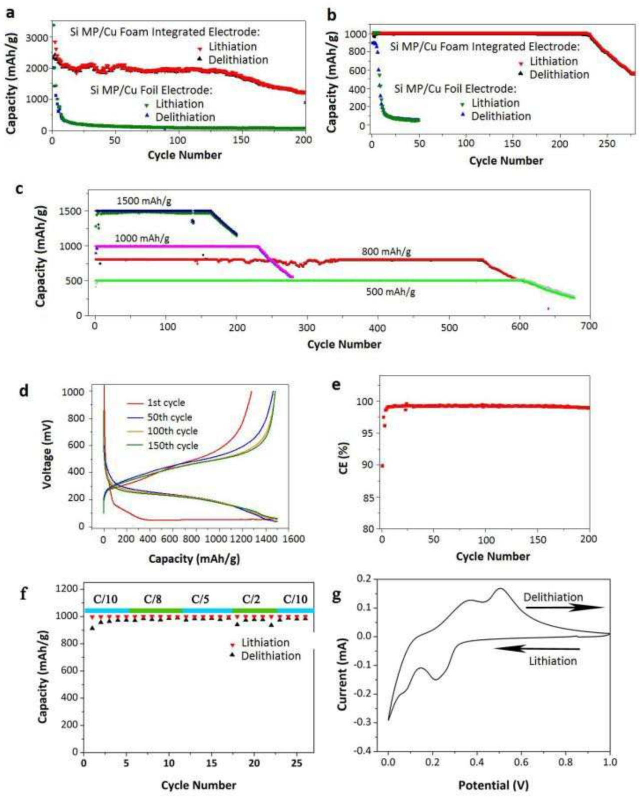

Fig. 3. Electrochemical characteristics of Si/Cu integrated electrodes. (a) Fully lithiation and delithiation performance of integrated electrode and traditional Si microparticle/copper foil electrode. (b) Constant lithiation and delithiation performance of 3D structure electrode vs tradition one. (c) The electrochemical performances of 3D structure electrodes by constant capacity lithiation with various values. (d) The lithiation/delithiation voltage profile of the silicon/Cu integrated anode at first, 50th, 100th and 150th cycles by a constant capacity of 1500 mAh/g. (e) Coulombic Efficiency of Si. (f) The rate performance of integrated electrodes. (g) Cyclic voltammetry profiles of the integrated electrodes.

Moreover, while traditional Si microparticle electrodes can only cycles less than 5 cycles with 1000 mAh/g lithiation capacity (Figure 3b), the integrated electrodes can stably cycle more than 200 times without capacity decay at a constant capacity of 1000 mAh/g with a current density of 0.5 A/g (Figure 3b). After 220 cycles, the capacity of the integrated electrode decreased quickly. We believe that the capacity fading after 220 cycles is attributed to the volume change which causes the poor electronic contact to the current collector and the pulverization of Si powders and unstable SEI formation after repeated cycles. If we control the deformation of silicon particles at a lower level by applied less lithiation capacity, the stability of the electrode can be improved reaching a longer cycling life. We show that the integrated electrode can maintain a capacity of 1500 mAh/g and 800 mAh/g for more than 170 and 550 cycles, respectively. We tested the electrode under a lower constant capacity of 500 mAh/g and reached more than 600 stable cycles (Figure 3c). Galvanostatic lithiation/delithiation profiles of the integrated electrode are shown in Figure 3d. As seen in the voltage profiles, the first cycle lithiation potential showed a plateau profile at 0.1- 0.0 V, consistent with the behaviour of crystalline Si.[12, 29] Note that the capacity of the electrode is calculated based on the mass of Si micronparticles, the extra mass of the metal substrate are not accounted. The areal density of copper foam is about 50 mg/cm^2, higher than that of copper foil (20 mg/cm^2). To further improvement of the overall capacity of the electrode, light density metal forms with higher porosity and/or hierarchical structured metal frameworks can be used.[37, 39] Coulombic efficiency (CE) is one key parameter for practical applications of silicon based anode. The CE of our SiMP/Cu integrated electrode cycled at a current density of 0.5 A/g with constant lithiation capacity of 1000 mAh/g is shown in Figure 3e. The electrode has a CE of 89.8 % for the first cycle with constant lithiation capacity of 1000 mAh/g, and 87.5 % during fully lithiation/delithiation. The CE for the first cycle is higher than Si nanowire or nanoparticle electrodes,[7, 12, 18] and comparable to traditional graphite anode.[3] In later cycles, the CE of the electrode was around 99.2 %. Figure 3f shows the rate performance of integrated electrodes at a constant capacity of 1000 mAh/g. The electrodes exhibit stable electrochemical performance when the current densities increase from 0.1 A/g to 0.125 A/g, 0.2 A/g and 0.5 A/g. Figure 3g displays the first cyclic voltammetry curves of the integrated electrode in the potential window of 0-1 V at a scan rate of 0.1 mV/s. It shows lithiation peaks at 0.21 and 0.07 V, and delithiation peaks at 0.35 and 0.5 V. These peaks and shape are consistent with the results reported for micrometre electrodes.[38, 40]

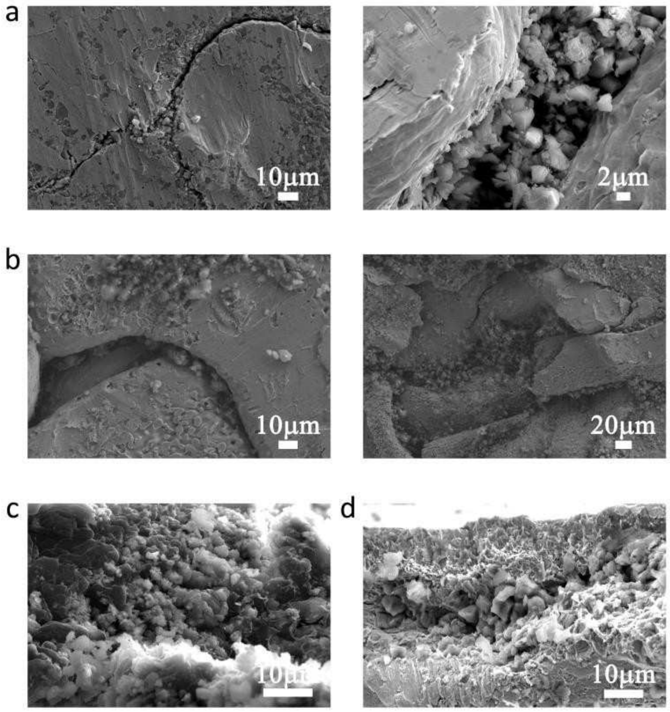

Fig. 4. SEM image of the composite electrode before (a) and after (b) 200 times of electrochemical cycling. (c) SEI coating on the particles after cycling. (d) Cross-section of the integrated electrode after cleaning the SEI.

We observed the 3D structure electrode before and after electrochemical cycling by SEM. Clearly, silicon particles have been successfully sealed in the metal foam and after continuous lithiation and delithiation few particles escaped from the 3D current collector. Figure 4 shows that after the electrochemical cycles, both the particles stuck in the cracks on the electrode surface and the particles embedded in the copper foam (Figure 4a) are trapped tightly (Figure 4b). This design cannot prevent the unstable SEI formation (Figure 4c). After we clean the SEI by dilute hydrochloric acid solution, particles are still sealed. The SEM images and electrochemical cycling performance confirm that the design of trapping the active electrode material inside a 3D porous metal current collector can successfully improve the cycling performance of battery electrodes.

Conclusions

To conclude, we designed a new electrode structure by integrating 3D current collector with active materials together and achieved significantly improved cycling stability of silicon according to such design. This solution-based synthesis method and its compatibility with roll-to-roll coating methods make this system readily scaled for large area electrode. Our new design of the integrated electrode may also be useful for other materials that suffer from mechanical issues during electrochemical reactions, including other alloy type anode and sulfur cathode materials for Li-ion batteries.

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Notes and references

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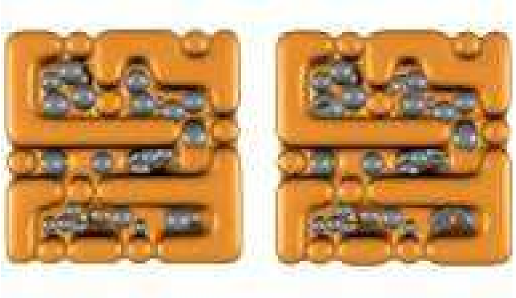

Improve the electrochemical performance by trapping micron-sized silicon particles inside the metal foam current collector in Li-ion batteries.